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AN INFRARED STUDY OF ISOTOPIC EXCHANGE DURING  
METHANATION OVER SUPPORTED. (U) AUBURN UNIV AL DEPT OF  
CHEMISTRY M A HENDERSON ET AL. 07 JAN 85 TR-3  
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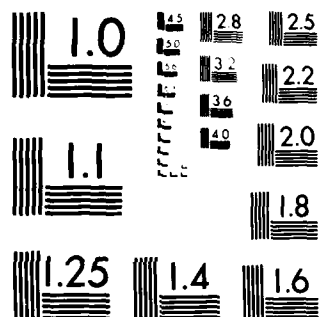
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AN INFRARED STUDY OF ISOTOPIC EXCHANGE DURING METHANATION OVER SUPPORTED RHODIUM CATALYSTS; AN INVERSE SPILLOVER EFFECT

ABSTRACT

(U) INFRARED SPECTROSCOPY HAS BEEN EMPLOYED TO STUDY THE REDUCTION OF CARBON DIOXIDE ON SUPPORTED CATALYST FILMS. THE INVESTIGATION INCLUDED ISOTOPIC LABELING USING DEUTERIUM AS THE REDUCTION GAS. ISOTOPIC EXCHANGE WAS OBSERVED FOR BOTH CARBON DIOXIDE/D2 AND METHANE/DEUTERIUM MIXTURES. THE MECHANISM OF THIS ISOTOPIC EXCHANGE INVOLVES MIGRATION OF HYDROGEN FROM THE SUPPORT TO THE RHODIUM SITES, AN INVERSE SPILLOVER EFFECT. A KEY INTERMEDIATE IN THE DISSOCIATION OF CARBON DIOXIDE ON THE SUPPORTED RH FILMS WAS A CARBONYL HYDRIDE SPECIES.

CARBON DIOXIDE

USE CARBON DIOXIDE

DISSOCIATION OF CARBON DIOXIDE

USE CARBON DIOXIDE

DISSOCIATION

INVERSE SPILLOVER EFFECT

USE INVERSION

SPILLING

METHANE DEUTERIUM MIXTURES

USE DEUTERIUM

METHANE MIXTURES

REDUCTION GAS

USE GASES

REDUCTION

SUPPORTED CATALYST FILMS

USE CATALYSTS

FILMS

CARBON DIOXIDE D2

POSTING TERMS ASSIGNED

DEUTERIUM

USE DEUTERIUM

INFRARED SPECTROSCOPY

USE INFRARED SPECTROSCOPY

ISOTOPIC EXCHANGE

USE EXCHANGE

ISOTOPES

MIGRATION OF HYDROGEN

USE HYDROGEN

MIGRATION

RHODIUM SITES

USE RHODIUM

SITES

SUPPORTED RHODIUM CATALYSTS

USE CATALYSTS

RHODIUM

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\* Isotope exchange - co.  
Reduction (Chemistry) - co.  
Chemical dissociation - co.  
Carbonyl compounds - co.  
Hydrides - co.

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An Infrared Study of Isotopic Exchange During  
Methanation Over Supported Rhodium Catalysts;  
An Inverse Spillover Effect

by

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An Infrared Study Of Isotopic Exchange During Methanation Over Supported Rhodium Catalysts; An Inverse Spillover Effect

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Abstract

Infrared spectroscopy has been employed to study the reduction of carbon dioxide on supported catalyst films. The investigation included isotopic labeling using  $D_2$  as the reduction gas. Isotopic exchange was observed for both  $CO_2/D_2$  and  $CH_4/D_2$  mixtures. The mechanism of this isotopic exchange involves migration of hydrogen from the support to the Rh sites, an "inverse spillover effect". A key intermediate in the dissociation of  $CO_2$  on the supported Rh films was a carbonyl hydride species.

deuterium

methane

carbon dioxide

rhodium

\*Author to whom correspondence should be addressed.

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## Introduction

A substantial amount of effort in these laboratories has been devoted recently to the study of the hydrogenation of carbon dioxide over supported rhodium catalysts. Of considerable interest and importance in this reaction is its likely first step, the dissociation of  $\text{CO}_2$  on the supported Rh. The dissociation of  $\text{CO}_2$  on Rh, or lack thereof, is a controversial topic at this time, with Somorjai and coworkers favoring a high dissociation probability ( $10^{-1}$ ) at 300 K,<sup>1</sup> while Weinberg<sup>2</sup> and Goodman and coworkers<sup>3</sup> suggest a low probability ( $10^{-15}$  and  $10^{-11}$  at 300 K, respectively). Very recently Solymosi and Kiss<sup>4</sup> have concluded that the dissociation probability at 300 K is low on clean Rh (111), but enhanced by the presence of small amounts of hydrogen gas or boron impurity. Henderson and Worley have reached a similar conclusion for supported Rh catalyst films.<sup>5</sup> Part of the preliminary evidence concerning  $\text{CO}_2$  dissociation on Rh/ $\text{TiO}_2$  and Rh/ $\text{Al}_2\text{O}_3$  obtained in these laboratories<sup>5</sup> was derived from isotopic labeling studies. The purpose of this letter is to present those data in more detail and to examine the hydrogen spillover phenomena for supported Rh catalyst films using infrared spectroscopy as a probe.

## Experimental

The supported Rh catalysts used in this study were prepared as thin films on  $\text{CaF}_2$  infrared windows by spraying slurries of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ , support material, water, and acetone onto the windows under mild heating to remove the solvents. Complete details concerning this method of sample preparation and subsequent reduction procedures have been presented previously concerning infrared studies of CO adsorbed on supported Rh<sup>6</sup> and the hydrogenation of CO over supported Rh.<sup>7</sup> The support materials were

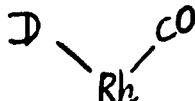
alumina (Degussa Aluminum Oxide C,  $100 \text{ m}^2\text{g}^{-1}$ ) and titania (Degussa Titanium Dioxide P25,  $50 \text{ m}^2\text{g}^{-1}$ ). The gases employed ( $\text{H}_2$ ,  $\text{D}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ) were of the highest purity obtainable from Matheson; the  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{CH}_4$  were passed through liquid nitrogen traps before use. The Pyrex infrared cell used in this investigation was similar to those employed in our earlier studies<sup>6,7</sup> except that it was designed such that it could be heated to ca. 523 K in situ in a Perkin-Elmer model 983 infrared spectrometer. The spectrometer was operated at a resolution of  $4.5 \text{ cm}^{-1}$  in the  $2000 \text{ cm}^{-1}$  region, with a Perkin-Elmer infrared data station being employed to facilitate data processing and storage. All experiments were run several times with the results obtained being entirely reproducible.

#### Results and Discussion

Figure 1 illustrates the effects of heating a mixture of  $\text{CO}_2$  and  $\text{D}_2$  over a 10% by weight Rh/ $\text{TiO}_2$  catalyst film. The film produced by the slurry-deposition technique mentioned in the Experimental Section was heated for 12 hr at 523 K at  $2 \times 10^{-6}$  Torr to remove as much hydrogen (from adsorbed  $\text{H}_2\text{O}$  and OH moieties) from the support as possible. However, it is well-established that this treatment at only 523 K is not sufficient to remove all hydrogen from the support. Then the film was reduced at 470 K by four successive doses of  $\text{D}_2$  at 70 Torr for time intervals of 5, 5, 10, and 20 min, each reduction cycle being followed by evacuation to  $10^{-5}$  Torr. Following evacuation to  $2 \times 10^{-6}$  Torr at 298 K, a 66 torr 1:4 mixture of  $\text{CO}_2$ : $\text{D}_2$  was introduced into the cell at 298 K, and spectrum 1a and Fig. 1 was recorded. The primary infrared bands observed in 1a (with the exception of the  $\text{CO}_2$  gas-phase band at  $2349 \text{ cm}^{-1}$ ) at 2704, 2626, and  $2527 \text{ cm}^{-1}$  can be attributed to the deuterated support (OD groups); any remaining



OH on the support was not of sufficient concentration to give observable OH infrared bands near 3600 or 1600  $\text{cm}^{-1}$ . A weak band in spectrum 1a at ca. 2020  $\text{cm}^{-1}$  is also evident, even at 298 K. This band can be assigned to a carbonyl deuteride species formed



as a result of  $\text{CO}_2$  dissociation. The corresponding carbonyl hydride band at low coverage for  $\text{CO}_2$  dissociation enhanced by  $\text{H}_2$  appears at ca. 2030  $\text{cm}^{-1}$ .<sup>5</sup> The reproducible 10  $\text{cm}^{-1}$  shift to lower frequency caused by the deuterium isotope effect is consistent with isotopic substitution two bonds removed from the CO moiety. It should be noted that Solymosi and coworkers first suggested the existence of such a carbonyl hydride species during  $\text{CO}_2$  dissociation.<sup>8</sup> We believe that the isotope effect observed in this study confirms the suggestion of Solymosi and coworkers, and thus negates the arguments of Iizuka and Tanaka<sup>9</sup> which essentially stated that bands observed in the 2020-2040  $\text{cm}^{-1}$  region of the infrared spectra of dissociated  $\text{CO}_2$  over supported Rh were due to a linear CO species at low coverage rather than a carbonyl hydride.

Following heating the sample at 503 K for 1 hr, spectrum 1b was recorded. The sharp band at 2258  $\text{cm}^{-1}$  can be assigned to a C-D stretching mode of gas-phase  $\text{CD}_4$ ,<sup>10</sup> the expected methanation product. A band at 996  $\text{cm}^{-1}$  could also be resolved using data subtraction which can be attributed to  $\text{CD}_4$ . The carbonyl deuteride band is shifted to higher frequency (2029  $\text{cm}^{-1}$ ) due to higher coverage of this species; the corresponding carbonyl hydride band for a sample treated identically, except using  $\text{H}_2$  instead of  $\text{D}_2$ , appears at 2039  $\text{cm}^{-1}$ . Bands at 2778 and 2720  $\text{cm}^{-1}$  can be assigned to

vibrational modes for gas-phase  $D_2O$  and  $HDO$ , respectively.<sup>10</sup> Also present were small sharp bands at  $2988\text{ cm}^{-1}$  and  $2141\text{ cm}^{-1}$ . The  $2988\text{ cm}^{-1}$  band is indicative of the presence of a small amount of  $CHD_3$ . The  $2141\text{ cm}^{-1}$  band does not grow in intensity upon further heating and is removed upon evacuation. At this time we can not propose an assignment for this band.

Spectra 1c and 1d show the further development of the bands mentioned above upon further heating at 503 K. New bands at 3010, 1234, 1089, and  $1035\text{ cm}^{-1}$  can be assigned to vibrational modes for gas-phase  $CH_2D_2$ . Upon evacuation at 298 K, spectrum 1e was obtained showing only the carbonyl deuteride surface species and broad bands indicative of a deuterated support. It should be noted that an analogous series of experiments for 10% Rh/ $Al_2O_3$  gave the  $CD_4$ ,  $CHD_3$ , and  $CH_2D_2$  products, but at a slower rate. Also a 0.5% Rh/ $Al_2O_3$  catalyst film gave qualitatively the same results, although the 0.5% sample actually produced the isotopically labeled methanes at a slightly greater rate than did the 10% sample indicating that small Rh ensembles can be important in the methanation of  $CO_2$ .

In a similar set of experiments a 10% Rh/ $TiO_2$  film reduced with  $D_2$ , heated at 523 K in the presence of 70 Torr  $D_2$  for 21 hr, and then evacuated at 298 K to  $1 \times 10^{-6}$  Torr, was exposed to a 66 torr 1:4 mixture of  $CO_2:H_2$  at 298 K. At 298 K the infrared spectrum revealed no measurable OD bands, yet a broad band at  $1610\text{ cm}^{-1}$  characteristic of a hydrated (H) support appeared. Nevertheless, upon heating to 503 K for 3 hr, infrared bands at 2199 and  $1156\text{ cm}^{-1}$  characteristic of  $CH_3D$ , as well as those (3014 and  $1304\text{ cm}^{-1}$ ) for  $CH_4$ , were observed.

Figure 2 shows the infrared spectra for a series of experiments involving a  $CH_4/D_2$  mixture over a 10% Rh/ $TiO_2$  film. For these experiments the film was heated and reduced in  $D_2$ . Then 100 Torr of a 1:1 mixture of

CH<sub>4</sub>:D<sub>2</sub> was added at 298 K, and spectrum 2a was recorded. At 298 K only the 3014 and 1304 cm<sup>-1</sup> bands for CH<sub>4</sub> are evident. However, after heating to 503 K for 30 min (2b) and 6 hr (2c), bands at 2986, 2258, 2199, 1234, 1156, 1089, 1034, and 994 cm<sup>-1</sup> clearly indicate the presence of CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub>, CHD<sub>3</sub>, and CD<sub>4</sub>, in addition to CH<sub>4</sub>. Evacuation at 298 K led to the removal of all of these bands (2d). Similar results were obtained for a 0.5% Rh/TiO<sub>2</sub> film.

All of these experiments suggest that isotopic scrambling is occurring on the supported Rh films. To discover whether this scrambling was related to the Rh, or just the support materials, the CO<sub>2</sub> reduction experiments and the CH<sub>4</sub>/D<sub>2</sub> mixture experiments were repeated for TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> films containing no Rh. The resulting infrared spectra show no infrared bands characteristic of any of the methanes other than the CH<sub>4</sub> when a CH<sub>4</sub>/D<sub>2</sub> mixture was used at the temperatures employed in these experiments. Utiyama and coworkers<sup>11</sup> have reported that isotopic exchange in a CH<sub>4</sub>/D<sub>2</sub> mixture does not occur over TiO<sub>2</sub> until temperatures greater than 773 K. However, other workers have observed CH<sub>4</sub>/D<sub>2</sub> exchange over Al<sub>2</sub>O<sub>3</sub> at low temperature (near ambient).<sup>12-14</sup> The sample pretreatment procedures in these experiments all involved heating to temperatures in excess of 750 K in O<sub>2</sub> or air before the exchange was attempted. Evidently our mild pretreatment procedure did not activate either TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> for isotopic exchange. Thus, it is apparent that all isotopic exchange in these experiments was induced by the presence of the Rh on the supports.

We believe that isotopic exchange in these experiments is a direct result of H or D migration from the support material to the Rh atoms or clusters. Otherwise, CHD<sub>3</sub> and CH<sub>2</sub>D<sub>2</sub> could not be formed from a gaseous mixture of D<sub>2</sub> and CO<sub>2</sub> over the supported Rh films as in Fig. 1. There has

been much interest recently in hydrogen and deuterium "spillover" from metals to supports.<sup>15</sup> There have also been suggestions of "reverse spillover" of D<sub>2</sub> onto Pt from TiO<sub>2</sub><sup>16</sup> and "back spillover" of protons onto Pt from TiO<sub>2</sub>,<sup>17</sup> among other similar observations.<sup>18-21</sup> We prefer to term the phenomenon as an "inverse spillover effect", and to our knowledge, this is the first documented example of such an effect for supported Rh catalysts. Furthermore, we believe that the "inverse spillover effect" significantly enhances the dissociation of CO<sub>2</sub> on supported Rh catalysts in the absence of H<sub>2</sub> gas.<sup>5,22</sup>

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- (22) A referee has suggested that an alternative explanation for our observations is a water gas shift sequence in which D<sub>2</sub>O produced from deuteration of CO<sub>2</sub> exchanges with the support to produce HDO which then reacts with CO to give CO<sub>2</sub> and HD. The resulting HD would then react with CO<sub>2</sub> on Rh to produce the CHD<sub>3</sub> and CH<sub>2</sub>D<sub>2</sub> observed. While this explanation is possible, we believe that an inverse spillover effect is more plausible because of the substantial amount of the deuterated products observed in a reactor in which D<sub>2</sub> would be in tremendous excess relative to any HD produced. Also, we observe infrared bands for CHD<sub>3</sub> before those for HDO appear.

### Figure Captions

Figure 1. Infrared spectra of a 10% Rh/TiO<sub>2</sub> film (4.8 mg cm<sup>-2</sup>) following heating at 523 K for 12 hr at 2x10<sup>-6</sup> Torr, reduction in D<sub>2</sub> at 470 K, evacuation at 298 K to 2x10<sup>-6</sup> Torr, and then: (a) introduction of 66 Torr of a 1:4 mixture of CO<sub>2</sub>:D<sub>2</sub> at 298 K, (b) heating at 503 K for 1 hr, (c) heating at 503 K for 3 hr, (d) heating at 503 K for 4.5 hr, (e) following evacuation at 298 K.

Figure 2. Infrared spectra of a 10% Rh/TiO<sub>2</sub> film (5.1 mg cm<sup>-2</sup>) following reduction in D<sub>2</sub> at 470 K and evacuation at 298 K to 2x10<sup>-6</sup> Torr, and then: (a) introduction of 100 Torr of a 1:1 mixture of CH<sub>4</sub>:D<sub>2</sub> at 298 K, (b) heating at 503 K for 30 min, (c) heating at 503 K for 6 hr, (d) following evacuation at 298 K.

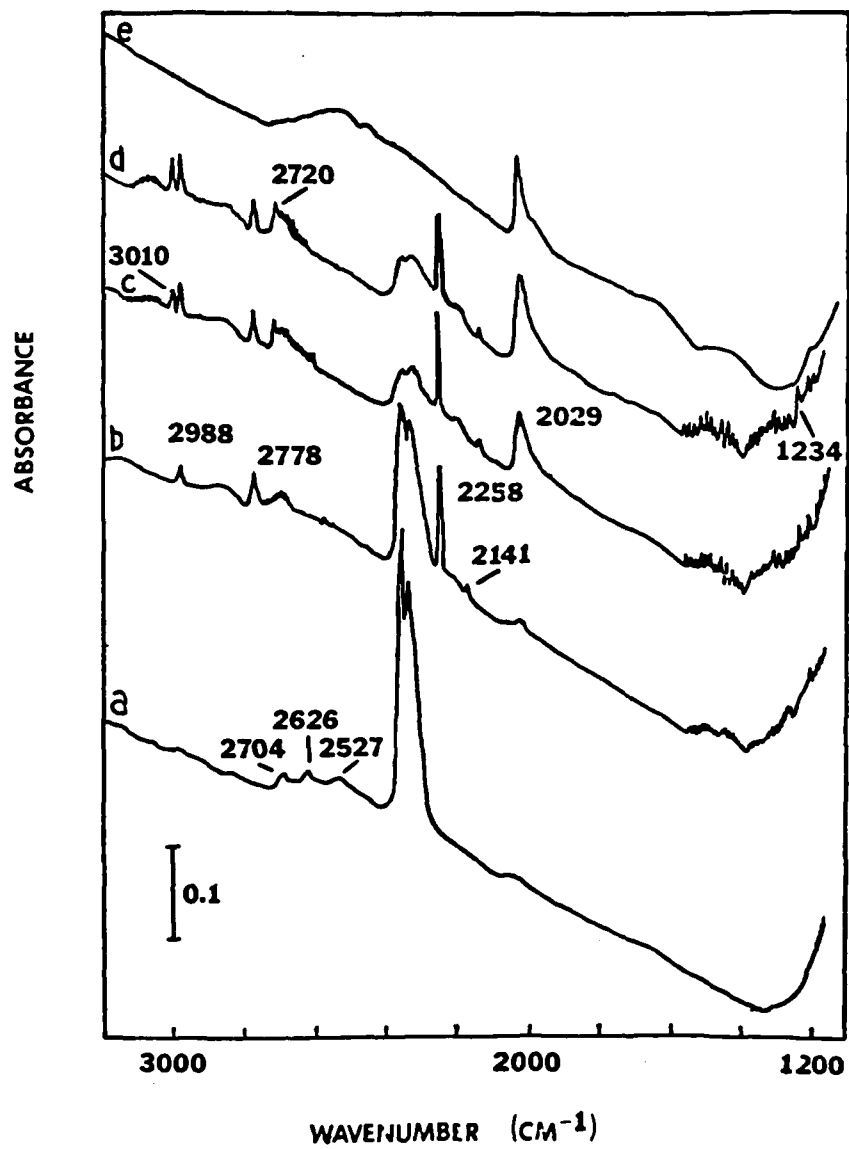
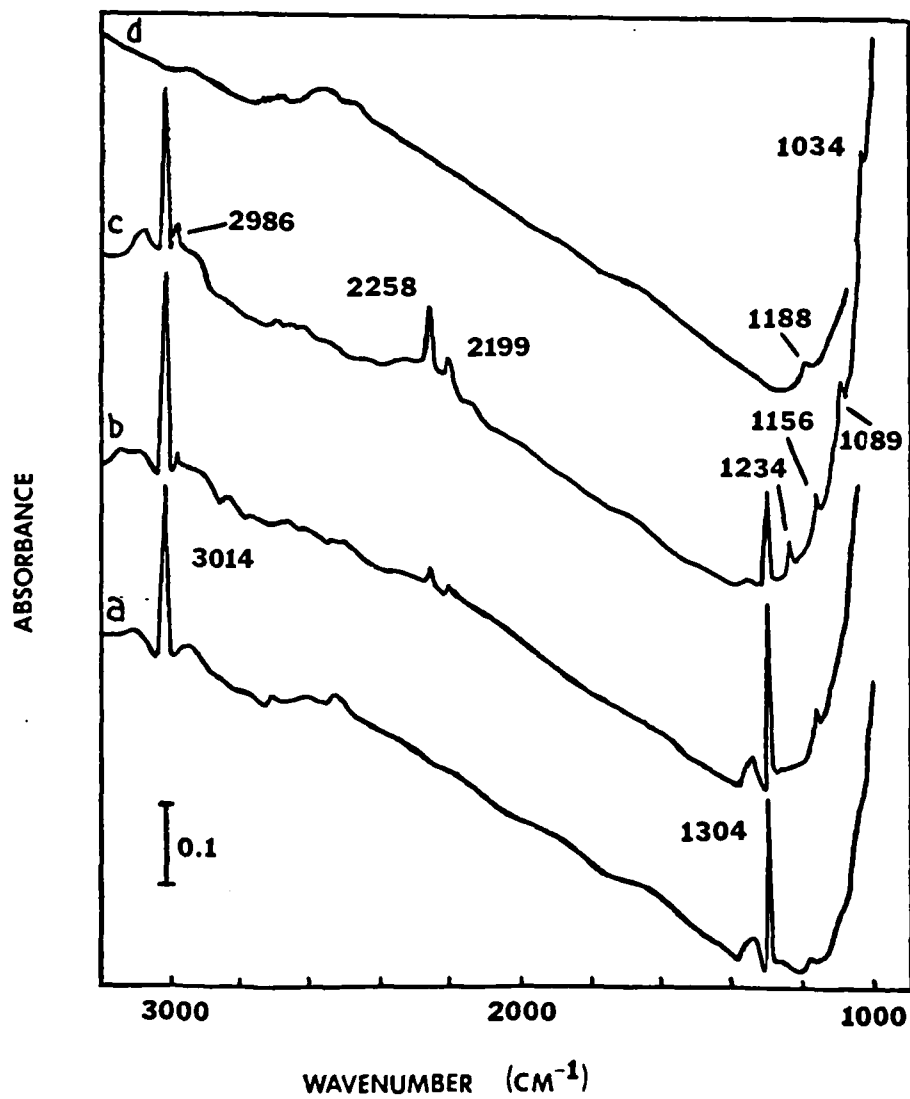


Fig. 2





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